Factors influencing carbon stabilization processes in volcanic ash Anthrosols (Tenerife Island, Spain)

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1. Introduction

There is a classical controversy concerning the mechanisms controlling the humification process in volcanic ash soils [1]. In general, it is considered that short-range silicates and amorphous oxides play an outstanding role in soil carbon stabilization. Nevertheless, despite the general agreement about the high potential for carbon sequestration in volcanic soils, the biogeochemical processes responsible for such an stabilization are not still completely understood. Whereas some authors have described a predominantly aromatic character of the humic acids (HAs) formed in allophane-containing soils, other authors have suggested that this aromaticity is but the effect of burning grass residues in the past (e.g. *Miscanthus sinensis*) [2], whereas the organic matter could be predominantly aliphatic as results of intense microbial activity in saturated anaerobic soil microcompartments, leading to the accumulation of alkyl, carbohydrate and protein-like constituents [3].

Another topic of Andosols refers to the progressive loss of its andic properties after extensive agricultural management. In fact, several authors have suggested that cultivation could result into enhanced exposure to sunlight and rapid desiccation of the topsoil, which would favour crystallization of amorphous oxides (allophane or imogolite) into crystalline clay-type minerals [4]. However, the general occurrence of these phenomena should be carefully considered since these data have been reported for tropical environments with large precipitation (> 1,700 mm) and heavy dry season, which is not the case with Canary Islands, where there exists a constant moisture provided by the condensation of trade winds. In order to shed some light about the above processes in soils at Tenerife Island, a total of 30 HAs extracted from andic and non-andic soils were analyzed.

2. Materials and methods

The sampling sites were representative for different types of vineyards on volcanic materials, corresponding to: i) soils with andic character in the Northern side of the Island, ii) soils covered with a pumice bed in the Southern side of the Island, iii) clay soils in both sides of the

Island, and, iv) soils on allochthonous volcanic materials that at the past were transported by farmers from the highlands to the coast, and traditionally referred to as *sorribas*.

A set of physicochemical variables representing diagnostic criteria in volcanic soil classification systems [5] was analyzed, such as bulk density, organic carbon, amorphous minerals ($Al_o+{}^1/_2\ Fe_o$), organo-mineral complexes (Al_p/Al_o), pH, retention of P, and water holding capacity at atmospheric pressure and at 1500 kPa. The presence of crystalline minerals was analyzed by X-ray diffraction (XRD). Humic acids and extractable insolubilized humins (soil-matrix fixed HAs) were isolated by alkaline extraction; in the case of insolubilized humin treating the soil with 60 m*M* $Na_2S_2O_4$ and 1 *M* HF-HCl [6].

The elementary composition (%C, %H and %N) of HAs was determined with a Carlo Erba EA1108 microanalyzer and the atomic H/C and O/C ratios were calculated. The optical density was measured at 465 nm (E4) and used to assess the maturity of organic matter whereas the second derivative of the visible spectrum allowed measuring the concentration of fungal quinoid pigments [7]. Derivative infrared spectroscopy was used to identify the "lignin fingerprint" which is often characteristic in HAs from soils treated with recent inputs of manures and compost. ^{13}C nuclear magnetic resonance (^{13}C NMR) was used to assess the different carbon types (aromatic, aliphatic…) including the possible accumulation of black carbon. Analytical pyrolysis was carried out in a Pyrojector (SGE instruments) connected to a GC/MS system Finnigan Trace GC Ultra with a Trace DSQ mass spectrometer. The identification of the individual compounds released by pyrolysis was carried out by i) single ion monitoring of different homologous series, ii) low resolution mass spectrometry and iii) comparison with published and stored data (NIST and Wiley libraries). With the data obtained, Principal Component Analysis (PCA) was used to identify possible biogeochemical processes in Anthrosols subjected to different agriculture practices.

3. Results and discussion

The structural differences between the HAs suggested that the origin of the variability of the soil organic matter could be explained by the differential contribution of two non-excluding processes, respectively i) selective preservation of plant and microbial biomacromolecules and ii) accumulation of condensed, aromatic HAs with high structural complexity (measured as the Shannon diversity index). In fact, a set of soils (mainly non-andic and developed on pumites) showed HAs with a typical lignin pattern reflected both by resolution-enhanced infrared spectroscopy and by the typical methoxyphenol pattern after analytical pyrolysis, suggesting a weakly condensed macromolecular structure also evidenced by low optical

density and comparatively small amounts of fungal quinoid pigments. Other set of soils, with a remarkable allophanic character showed HAs with large condensation and aromaticity (high optical density and fungal pigments), and pyrograms with methoxyl-lacking aromatic compounds, including high yields of carbohydrate-derived and nitrogen compounds.

As a whole, the results suggested that allophanic soils accumulated comparatively high amount of soil organic carbon, with HAs of a large degree of aromaticity and structural condensation. However, it is worthy to mention that the most aromatic HAs did not occur just in allophanic soils, but in clay soils subjected to liming and probably affected by burnings in the past (Fig. 1).

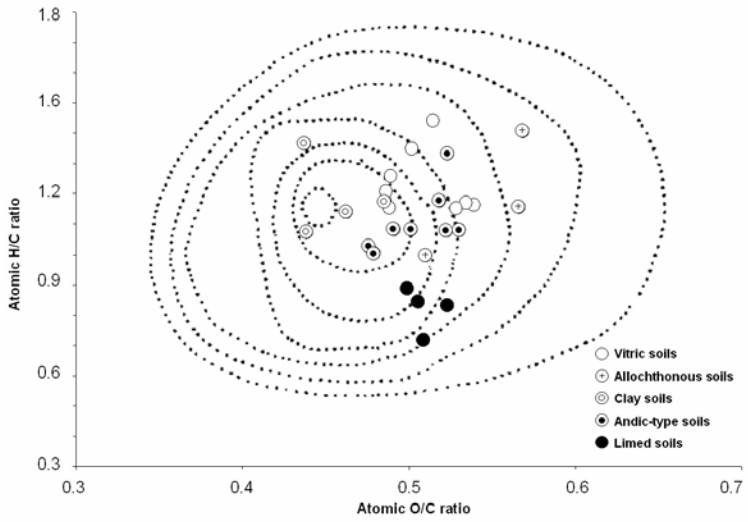

Figure 1. Graphical representation of the atomic H/C and O/C ratios (van Krevelen's diagram) of HAs from Anthrosols subjected to different agriculture practices. The data are plotted on a contour diagram of distribution and frequencies showing the natural variability of these atomic ratios in soil HAs.

The results obtained evidenced that the influence of agricultural management, which included inputs of transported allophanic materials in the past, have exerted a significant enhancement in organo-mineral complexes. This interaction is reflected in the performance of both soil carbon sequestration and soil agroecological quality. On the opposite hand, based on the difference between the mineralogical and the organic composition in the Anthrosols studied, we suggested that the weak humification processes observed in soils with a pumice bed, is due to the lack of reactive colloidal mineral, indispensable for the formation of the soil reactive matrix, while the periodic application of raw organic amendments favours the rapid mineralization of organic matter in these sandy soils, precluding the formation of humic substances.

4. Conclusions

In the volcanic soils under study, carbon stabilization is not only controlled by strong mineral interactions in part conditioned by volcanic ash transported to Anthrosols but also by intense perturbations associated to soil management practices including periodic input of manures and grass residues, and the effect of fire in the past. This suggest the possibility to control the humification processes by the farmer action, which—in the study zone—may represent the major source of variability on soil organic matter characteristics, with a stronger effect than that expected from the natural soil-forming factors.

References

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